

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-248561

(43)Date of publication of application : 27.09.1996

(51)Int.Cl.

G03C 1/675

C08K 5/15

C08K 5/42

C08L 25/18

C08L 33/12

(21)Application number : 07-049588

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(22)Date of filing : 09.03.1995

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(54) PHOTOREACTIVE COMPOSITION, ACID-REACTIVE HIGH POLYMER COMPOSITION CONTAINING THE SAME AND ACID-REACTIVE RESIN LAYER

(57)Abstract:

PURPOSE: To obtain a photoreactive composition having improved photosensing speed through amplifying photochemical reaction by using as the components of the composition, a photo- acid-generating agent that generates acid with the effect of light and an acid-breeding agent that newly generates acid with the acid generated by the photo-acid-generating agent.

CONSTITUTION: This composition consists of a photo-acid-generating agent that generates acid with the effect of light and an acid-breeding agent that newly generates acid with the acid generated by the photo-acid-generating agent. Namely, by using a combination of the acid-breeding agent that newly generates acid with the catalytic effect of acid and the photo- acid generating agent, for example, one acid molecule is generated and, one molecule of the acid-breeding agent is decomposed by one acid molecule generated with the photo-acid- generating agent into newly formed one or more acid molecules and therefore, the one or more acid molecules are bred into two or more acid molecules by each acid-catalytic reaction and thus, these reactions are caused in a chainlike manner to increase the acid molecules in a geometrical-progressional manner. By adding the acid-breeding agent having such characteristics, the amount of acid is rapidly increased and as a result, termination of the acid-catalytic reaction due to any basic substance and disappearance of the acid by any side reaction can be prevented from occurring and thereby, the acid-catalytic reaction can be accelerated.

LEGAL STATUS

[Date of request for examination]

18.10.1999

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

3418946

[Date of registration]

18.04.2003

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] A photoreaction nature constituent which consists of a photo-oxide generating agent which generates an acid according to an operation of light, and an acid growth agent which newly generates an acid with an acid generated from this photo-oxide generating agent.

[Claim 2] An acid reactive polymer constituent characterized by making a photo-oxide generating agent which generates an acid according to an operation of light, and an acid growth agent which newly generates an acid according to an operation of this acid exist in a high polymer which mixed material which produces molecular structure change according to an operation of an acid, or a high polymer which combined residue which produces molecular structure change according to an operation of an acid.

[Claim 3] An acid reactivity resin layer characterized by providing the following An acid growth agent which newly generates an acid with an acid generated from said photo-oxide generating agent in a resin layer which consists of a high polymer which mixed material which produces molecular structure change according to an operation of an acid or a high polymer which combined residue which produces molecular structure change according to an operation of an acid, and a photo-oxide generating agent Two-layer structure which carried out the laminating of the different resin layer from the aforementioned resin layer which consists of a high polymer which mixed material which produces molecular structure change according to an operation of a newly generated acid, or a high polymer which combined residue which produces molecular structure change according to an operation of an acid

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the acid reactive polymer constituent and acid reactivity resin layer containing this photoreaction constituent further about the photoreaction constituent which raised sensitization speed by combining the material (it being hereafter called an acid growth agent) which newly generates an acid with the generated acid with the material (it being hereafter called a photo-oxide generating agent) which generates an acid in an operation of light.

[0002]

[Description of the Prior Art] Light energy is absorbed conventionally and it is used in the direction chemical between intramolecular or a molecule or of versatility [material / which has the photosensitive function which produces a physical change]. For example, in many fields, it is used and using as an image formation material which detects optically the chemical structural change produced by the photoreaction, or using as a surface coating processing material which performs surface treatment by the photo-curing of a monomer or a prepolymer etc. is put in practical use. However, the sensitization speed in the material which has these photosensitive functions, a sensitization wavelength field, and definition are various, and the material which has a suitable property according to the purpose is chosen.

[0003] Although silver salt sensitive material was used more widely in ancient times as a material which has a photosensitive function, the photopolymer which uses polymeric materials as a principal component reaches far and wide as extensive and the high sensitivity image formation material in which high definition is shown, and it came (refer to the volume Yamaoka Tsugio and for Gentaro Matsunaga, "photopolymer technology", and Nikkan Kogyo Shimbun (1988)) to be used in recent years. [as / in photoengraving-process technology etc.] The macromolecule system photosensitivity material is not only excellent in definition, but can set up a wide range sensitization wavelength field by selection of the photoreaction. Moreover, it has many advantages of being able to manufacture comparatively cheaply. However, sensitization speed is very low in comparing with a silver salt photosensitivity material, and also although it is called the high sensitivity macromolecule system photosensitivity material, the present condition is not amounting to 1/1000 of the sensitization speed which a silver salt material's shows.

[0004] In order to raise the sensitization speed of a macromolecule system photosensitivity material, various attempts have so far been made. It is the photopolymerization system to which having been most widely set as the object of development carries out the polymerization of many vinyl monomers continuously by making into an initiator the radical kind generated in an operation of light. However, since the oxygen in air and the radical kind which reacts easily are growth kinds, it ends, without completing sufficient chain reaction. Moreover, with advance of a radical polymerization reaction, diffusion of a monomer is quickly controlled for the network structure within the macromolecule matrix formed rapidly, and a polymerization cannot be completed. For such a cause, essential threshold value exists in the sensitization speed of a photopolymerization system.

[0005] Creation of various macromolecule system photosensitivity materials was attained by generating an acid in an operation of light and on the other hand, combining not only the cationic polymerization that makes this acid a catalyst but various acid catalyzed reactions. Although high sensitivity is expected since there is no halt effect of the reaction by oxygen unlike a radical polymerization, sensitization speed of the present condition is rather lower in cationic polymerization, than a radical polymerization system in fact for the moisture in air, or network structure formation. Moreover, let it be a principle to heat-treat, after generating an acid with light, and to carry out induction of the acid catalyzed reaction with the macromolecule system photosensitivity material incorporating an acid catalyzed reaction. For this reason, this kind that makes a photoresist a main use gestalt of macromolecule system photosensitivity material is called the chemistry amplification mold photoresist. However, the present condition is that sensitization speed is less than a radical polymerization system, and improvement in a fast sensitization speed has still been called for.

[0006] Furthermore, by using an optical radical polymerization and optical cationic polymerization, or combining the both, the resin constituent which hardens a film-like resin coat to a high degree of hardness by optical exposure is also large liquefied, and practical use is presented. Although the optical cationic polymerization system which does not receive the inhibition effect by the oxygen in air is widely set as the object of development research and development of the monomer and prepolymer suitable for the photo-oxide generating agent suitable for hardening or hardening is performed actively in recent years, improvement in a cure rate is called for for speeding up of a hardening production process. Furthermore, since hardening of the resin constituent and the thick coat which the

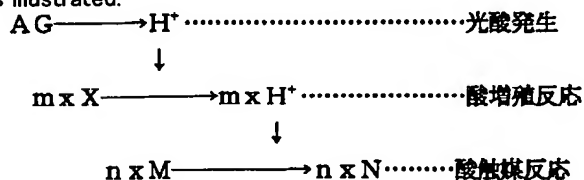
pigment which absorbs light distributed takes place only by the surface layer, the essential trouble that sufficient hardening is not brought about has resulted as it is not solved. Moreover, it thinks for the base component of the minute amount which floats in air to bring about a poisoning operation of a catalyst as a cause by which it will not become so high although the sensitization speed of the above-mentioned chemistry amplification mold photoresist uses the acid catalyzed reaction, or the acid catalyzed reaction in the inside of a macromolecule matrix triggers side reaction, and it is also considered that an acid catalyzed reaction stops for this reason.

[0007]

[Problem(s) to be Solved by the Invention] The result to which this invention person examined various the methods of solving such a situation radically, It is what completed a header and this invention for the photoreaction constituent which raised sensitization speed remarkably by combining the material which newly generates an acid with the generated acid with the material which generates an acid in an operation of light. The purpose of this invention offers the photoreaction constituent which was made to amplify photochemical reaction and raised sensitization speed remarkably.

[0008]

[Means for Solving the Problem] A photo-oxide generating agent in which a summary of invention of the 1st of this application generates an acid according to an operation of light, It is the photoreaction nature constituent which consists of an acid growth agent which newly generates an acid with an acid generated from this photo-oxide generating agent. A photo-oxide generating agent which generates an acid according to an operation of light in a high polymer which mixed material from which a summary of the 2nd invention produces molecular structure change according to an operation of an acid, or a high polymer which combined residue which produces molecular structure change according to an operation of an acid, It is the acid reactive polymer constituent characterized by making an acid growth agent which newly generates an acid according to an operation of this acid exist. A high polymer which mixed material from which a summary of the 3rd invention produces molecular structure change according to an operation of an acid, Or an acid growth agent which newly generates an acid with an acid generated from said photo-oxide generating agent in a resin layer which consists of a high polymer which combined residue which produces molecular structure change according to an operation of an acid, and a photo-oxide generating agent, The aforementioned resin layer which consists of a high polymer which mixed material which produces molecular structure change according to an operation of a newly generated acid, or a high polymer which combined residue which produces molecular structure change according to an operation of an acid is an acid reactivity resin layer which has two-layer structure which carried out the laminating of the different resin layer. Namely, by combining with a photo-oxide generating agent an acid growth agent which newly generates an acid according to an operation of an acid in this invention Since one acid is generated, and this acid disassembles an acid growth agent molecule and newly generates one or more acids from a photo-oxide generating agent according to an operation of light One or more acid-content children will increase at one reaction, it will become a total of two or more acid-content children, this reaction will arise continuously, and generating of an acid will increase in multiplying like rats. That is, by addition, an acid can also prevent a halt of an acid catalyzed reaction by increase, consequently alkali rapidly, and disappearance of an acid by side reaction can also prevent an acid growth agent with such a property, and an acid catalyzed reaction can be accelerated sharply. It is as follows when a principle of an above-mentioned reaction principle is illustrated.



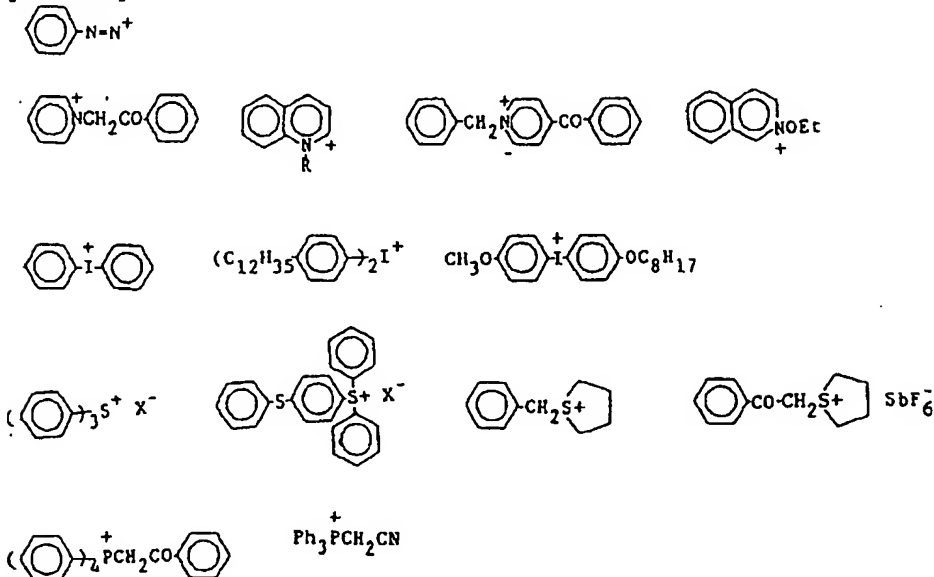
AG Photo-oxide generating agent; X Acid growth agent; M Acidolysis product; N The acidolysis products m and n are molecularity. An organic compound which increases such an acid was used, and a growth reaction which generates an acid in multiplying like rats was not known at all as an organic chemistry reaction until now, although it was similar to a nuclear fission reaction or explosive reaction. Although it is thermally stable as much as possible, an acid decomposes and an acid growth agent generates strong acid itself, it is the compound replaced by residue of a comparatively strong acid, and triggers an elimination reaction comparatively easily and generates an acid. Therefore, although it is stable under un-existing [of an acid] if this elimination reaction can be sharply activated by acid catalyzed reaction, under existence of an acid, it becomes possible to make thermal reaction generate an acid easily. By combining an acid growth agent with such a property with a photo-oxide generating agent, a photosensitive material whose sensitization speed improved by leaps and bounds became possible.

[0009] This invention is explained to details. As a photo-oxide generating agent which generates an acid according to an operation of light in this invention, a compound used for a chemistry amplification mold photoresist or optical cationic polymerization is used (a volume on organic electronics material study group, "imaging business refer to organic material", the *** exudation version (1993), and 187 - 192 pages). An example of a suitable compound for this invention is given to below. Moreover, in order to expand a sensitization wavelength field of these photo-oxide generating agents, a photosensitizer can also be made to live together suitably. With the acid active substance, an acid generated by photolysis of such material acts on an acid growth agent, and promotes generating of an acid. The following photo-oxide generating agents can be used. PF6- of aromatic series onium compounds, such as diazonium,

ammonium, iodonium, sulfonium, and phosphonium, AsF_6^- , SbF_6^- , and a CF_3SO_3^- -salt can be mentioned [1st]. A concrete example of an onium compound is shown below.

[0010]

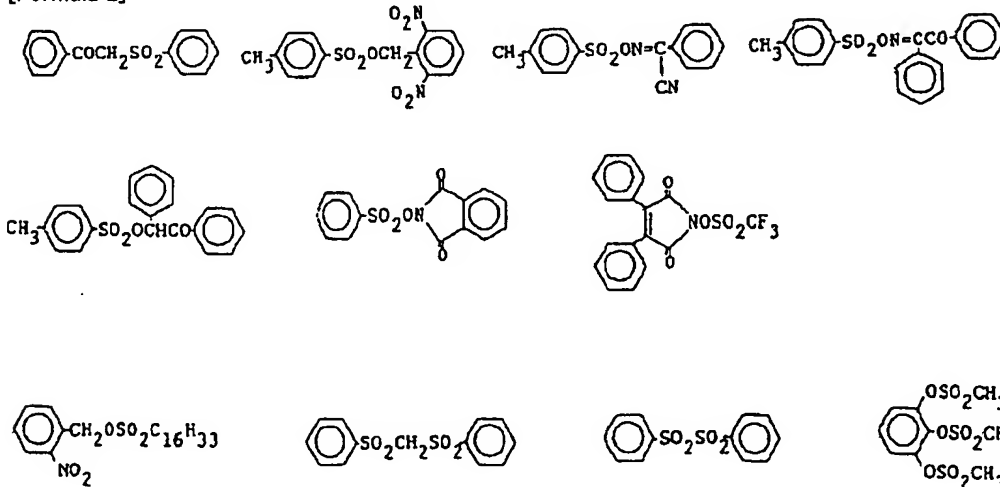
[Formula 1]



[0011] The sulfonation object which generates [2nd] a sulfonic acid can be mentioned. A concrete compound is illustrated below.

[0012]

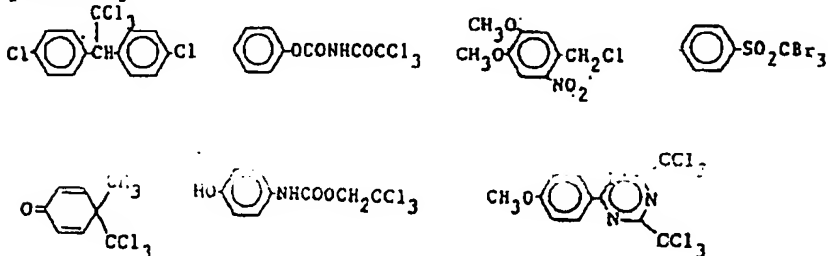
[Formula 2]



[0013] The halogenide which carries out optical generating of the hydrogen halide can also be used [3rd]. A concrete compound is illustrated below.

[0014]

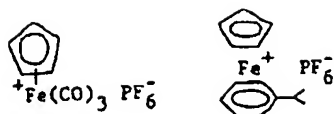
[Formula 3]



[0015] An iron allene complex can be mentioned to the 4th.

[0016]

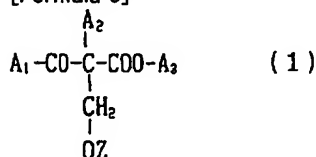
[Formula 4]



[0017] The acid growth agent used by this invention is the compound replaced by the residue of a comparatively strong acid, and is a compound which triggers an elimination reaction comparatively easily and generates an acid. Therefore, this elimination reaction can be sharply activated by the acid catalyzed reaction, and although it is stable under un-existing [of an acid], under existence of an acid, it becomes possible to make thermal reaction generate an acid easily. By combining an acid growth agent with such a property with a photo-oxide generating agent, the photoreaction nature constituent whose sensitization speed improved by leaps and bounds became possible. An acid catalyzed reaction decomposes and an acid (it is ZOH at the following general formulas) is generated again. One or more acids are increasing in number at one reaction, and a reaction progresses accelerative with advance of a reaction. In order for the generated acid itself to carry out induction of the autolysis, reinforcement of the acid generated here is set to an acid dissociation constant and electric dissociation exponent, and is three or less, and it is desirable that it is two especially or less. An autolysis cannot be caused if it is an acid weaker than this. As such an acid, dichloroacetic acid, a trichloroacetic acid, methansulfonic acid, ethane sulfonic acid, benzenesulfonic acid, p-toluenesulfonic acid, a naphthalene sulfonic acid, triphenyl phosphonic acid, etc. can be raised. Specifically, the following compounds can be illustrated. The organic-acid ester compound expressed [1st] with a general formula (1) can be mentioned.

[0018]

[Formula 5]

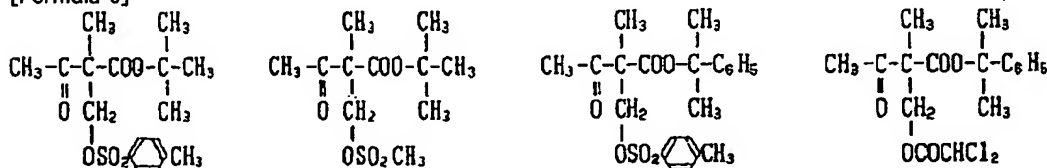


[0019] (A1 shows the alkyl group or aryl group from C1 to C6 among a formula, A2 shows the alkyl group from C1 to C6, and A3 is screw (p-alkoxy phenyl) methyl) A radical, a 2-alkyl-2-propyl group, a 2-aryl-2-propyl group, a cyclohexyl radical, or a tetrahydropyranyl group is shown, and Z shows the residue of the acid shown by ZOH whose acid dissociation constant (electric dissociation exponent) is three or less.

If an acid acts on this compound, an ester group decomposes and it becomes a carboxylic acid, and after this raises a decarboxylic acid further, an acid (ZOH) will **** easily. Specifically, an example is shown below.

[0020]

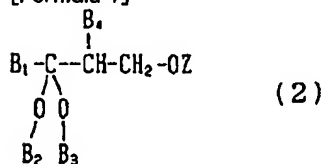
[Formula 6]



[0021] Organic-acid ester with the acetal or ketal radical expressed [2nd] with a general formula (2) can be mentioned.

[0022]

[Formula 7]

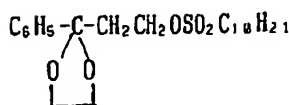
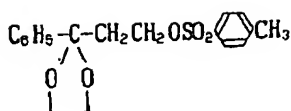


[0023] (Z has the same semantics as the above among a formula, B1 is a hydrogen atom, an alkyl group, or an aryl group, B-2 and B3 form ethylene or a propylene radical in methyl, an ethyl group, or both, and B4 shows a hydrogen atom or a methyl group)

An acetal or ketal decomposes in an operation of an acid, this compound serves as beta-aldehyde or a ketone, and ZOH is easily desorbed from it after this. A concrete example is shown below.

[0024]

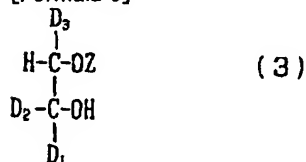
[Formula 8]



[0025] The organic-acid ester expressed [3rd] with a general formula (3) can be mentioned.

[0026]

[Formula 9]

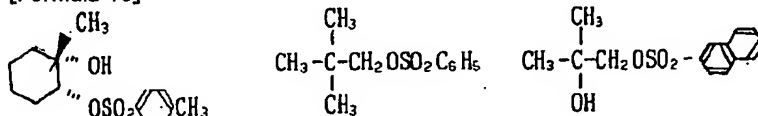


[0027] (Z has the same semantics as the above among a formula, D1 and D2 show a hydrogen atom, the alkyl groups from C1 to C6, or an aryl group, and D2 and D3 show the alkylene or substitute alkylene residue which forms alicycle-like structure on the alkyl group or both sides from C1 to C6)

After a hydroxyl group ****s, and this compound forms carbocation and carries out hydrogen migration according to an acid catalyst, it is presumed to be what ZOH generates. A concrete example is shown below.

[0028]

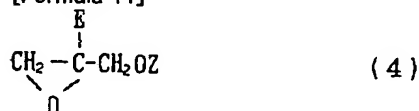
[Formula 10]



[0029] The organic-acid ester which has the epoxy ring expressed [4th] with a general formula (4) can be mentioned.

[0030]

[Formula 11]

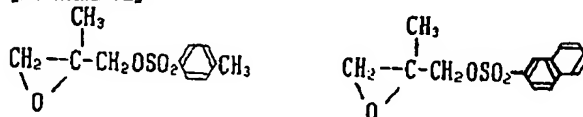


[0031] (Z has the same semantics as the above among a formula, and E shows the alkyl groups or phenyl groups from C1 to C6)

If an acid acts on this compound, a cation will be formed in beta-carbon with generation of the ring breakage of an epoxy ring, and what an organic acid generates as a result of hydrogen migration will be presumed. A concrete example is shown below.

[0032]

[Formula 12]

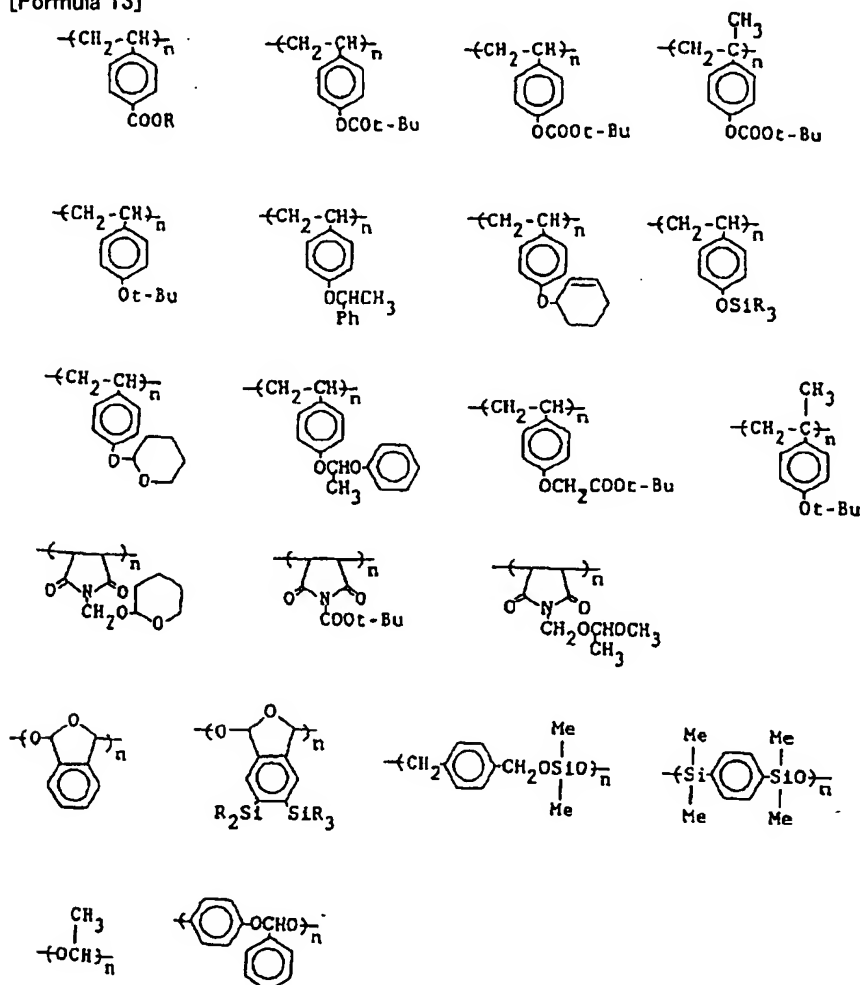


[0033] These compounds exist in stability at a room temperature, unless an acid acts. Although the acid strength more than fixed is needed in order to cause acid-catalyst disassembly of these compounds, it is desirable that it is about two or less in an acid dissociation constant pka. If it is the acid dissociation constant beyond this, i.e., a weaker acid than this, the reaction of an acid growth agent cannot be triggered.

[0034] Next, the high polymer which mixed the material (acid reactivity molecule) which produces molecular structure change according to an operation of the acid in which the above-mentioned photoreaction constituent is made to exist, or the high polymer which combined the residue which produces molecular structure change according to an operation of an acid is explained. In addition, the material or residue which produces molecular structure change is only called an acid reactivity molecule or acid reactivity residue. The example of a high polymer which mixes, or joins together and becomes about the acid reactivity molecule used suitable for this invention is shown (the volume on organic electronics material study group, "imaging business refer to organic material", the

**** exudation version (1993), and 199 - 201 pages). many use the reaction of the deprotection radical in synthetic organic chemistry — **** (T. refer to W.Greene, Protective Groups in Organic Synthesis, and John Wiley & Sons (1981)) — a concrete example is shown below. The high polymer which has acid reactivity residue in a side chain or a principal chain can be mentioned to the 1st. As acid reactivity residue, the phenol nature or N-methylol nature hydroxyl group protected by the 2nd class, the 3rd class ester, the tetrahydropyranyl ester, the 3rd class ester of carbonic acid, trialkylsilyl group, and tetrahydropyranyl group of a carboxylic acid is used suitably. Since a deprotection reaction occurs and a polar high carboxylic acid and a polar high phenol generate these according to an operation of an acid, the exposure section is solubilized in a polar solvent or an alkali aqueous solution. High sensitivity sensitive material is one of things using such a property. As the example of a concrete compound, [0035]

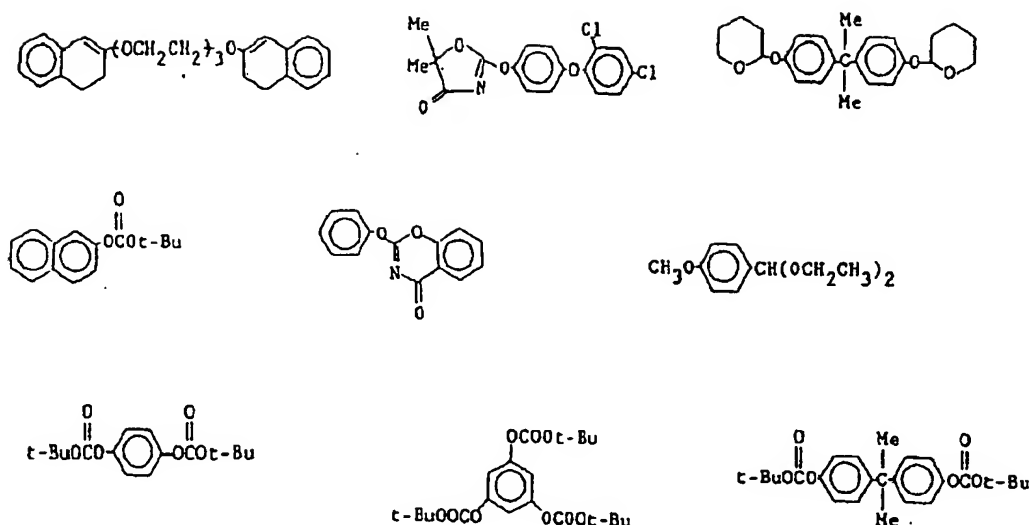
[Formula 13]



[0036] The high molecular compound containing an acid reactivity low molecular weight compound is in the 2nd. Here, an acid reactivity low molecular weight compound has the effect of reducing the solubility of a resin compound, and is called a dissolution inhibitor. As a dissolution inhibitor, phenols, a pinacol derivative, etc. which were protected by an acetal compound, a ketal compound, the 3rd class ester of a carboxylic acid, tetrahydropyranyl ester, the 3rd class ester of carbonic acid, the trialkylsilyl group, or the tetrahydropyranyl group can be mentioned. As a resin compound containing these dissolution inhibitors, novolak resin, Pori (p-hydroxystyrene), a methacrylic-acid copolymer, N-methylol maleimide copolymer, etc. can be raised. Although a low molecular weight compound has the effect which checks the solubility over the alkali aqueous solution of these resin, by decomposing in an operation of an acid, this dissolution depressor effect is lost and a macromolecule serves as alkali solubilization. A concrete dissolution inhibitor is illustrated below.

[0037]

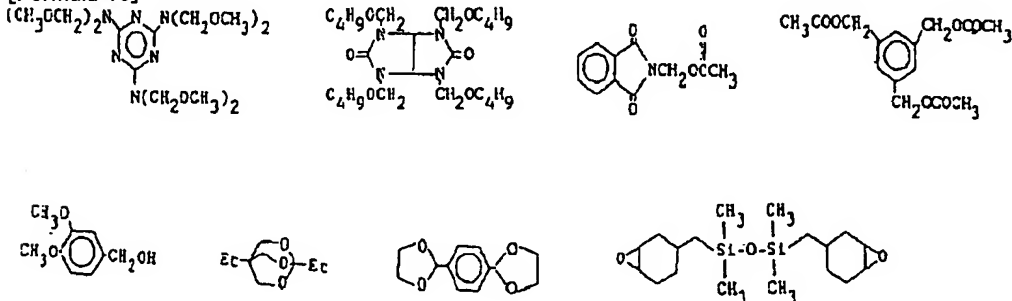
[Formula 14]



[0038] The condensation reaction by the acid catalyzed reaction is used [3rd] for the crosslinking reaction of a macromolecule. As residue which forms a cation and causes a condensation reaction by the acid catalyst, a benzyl alcohol derivative, a melamine derivative, N-methylol imide derivative, an acetal derivative, a vinyl ether derivative, etc. can be raised. Moreover, as generated KAOCHIN and residue which reacts, a phenol, alcohol, etc. can be mentioned and polymer ** of the macromolecule which has such residue, for example, the polymer of p-hydroxystyrene, novolak resin, and hydroxyethyl methacrylate is used suitably. The compound which causes a condensation reaction is illustrated below.

[0039]

[Formula 15]



[0040] Moreover, since the macromolecule having this condensation nature residue and phenyl residue causes bridge formation by the acid catalyst by itself, it is convenient for this invention. A macromolecule with the residue which carries out [4th] a polymerization according to an acid catalyst is used. As cationic polymerization nature residue, an epoxy group, oxetane residue, a vinyl ether radical, an isopropenyl phenyl group, annular orthochromatic ester, etc. can be raised. The constituent set to the 5th from a cationic polymerization nature monomer or a prepolymer is also used. As a cation nature monomeric unit, an epoxy group, an oxetane radical, a vinyl ether radical, and annular orthochromatic ester are used. It is desirable to mix with a vinyl system polymer and to use these monomers or prepolymers as the filmy material of self-support nature.

[0041] Subsequently, the adjustment method of the photopolymer constituent of this invention is described below. To the high molecular compound which is acid reactivity, the resin or itself containing low-molecular material with an acid reactivity unit adds 0.5 - 20% of the weight of a photo-oxide generating agent, and 0.1 - 20% of the weight of an acid growth agent to it. Since many of above-mentioned photo-oxide generating agents generate a radical kind with an acid, it can also mix with a radical polymerization nature monomer or a prepolymer with the acid active substance. Furthermore, a pigment, a color, etc. may be added suitably.

[0042] In order to distribute to homogeneity, it is desirable to dissolve each liquefied. It exposes, after making these constituents into the shape of a film, and the acid as a latent image is generated. Subsequently, while performing heating (postbake) processing and urging a chain of decomposition of an acid growth agent, an acid catalyzed reaction causes a structural change of the acid active substance. although the conditions of heat-treatment are changed according to the class of residue [activity / acid / exposure energy and / to be used], the class of macromolecule, etc. — heating temperature — the range of 60 to 150 degrees — it is the range of 80 to 130 degrees more preferably. Heating time is 5 minutes from 30 seconds more preferably from 10 seconds for 10 minutes. If heating time is short more than this, an acid catalyzed reaction will not fully be triggered, in the time amount exceeding this range, an acid growth agent may trigger side reaction, and productivity is missing. The resin or itself containing the acid active substance uses change of the physical properties before and behind the exposure accompanying a structural change of the resin which is acid reactivity, and heat-treatment, for example, solubility, a

degree of hardness, thickness, viscosity, gassing, etc. Furthermore, it can divide into the resin layer which contains a photo-oxide generating agent in this invention, and the resin layer containing an acid growth agent, and can consider as two-layer structure. Next, this invention is explained still more concretely with an example.

[0043]

[Example] The synthetic example of the typical acid growth agent which can be first used by this invention is shown as an example of reference.

It was made to react to the 2-methyl-3-keto butanoic acid tert butyl ester which example of reference 1 acetoacetic-acid tert-butyl ester was made to react with a methyl iodide, and obtained it under existence of the sodium hydride in THF with formalin in ethanol under existence of a potassium hydroxide. The 2-hydroxymethyl-2-methyl-3-keto butanoic acid tert butyl ester generated at 40% of yield was made to react with p-tosyl chloride under existence of triethylamine in dichloromethane, and 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester was obtained as oily matter. The product was refined by silica gel column chromatography -

m. p.52-53-degree-C1 H-NMR (CDCl3)

delta (ppm):1.38(s,3H,-COC(CH3)CO-),1.40(s,9H,-C(CH3)3),2.15(s,3H,CH3CO-),2.47(s,3H,Ar-CH3),4.28 (ABq,J=10Hz,2H,-CH2-OSO2-),7.38(d,J=7.7Hz,2H,Ar-H),7.77(d,J=7.7Hz,2H,Ar-H)

IR(cm⁻¹): 1738 (>C=O of ester) 3000, 1719 (>C=O)

Elemental-analysis C17H24O6Scalc. C:57.29% H:6.79% S:9.00%found C:57.18% H:6.90% S:8.84% [0044] Like example of reference 2 example 1, methansulfonic acid chloride was used instead of p-tosyl chloride, and 2-methyl-2-methane sulfonyloxy-3-keto butanoic acid tert butyl ester was obtained as oily matter.

1H-NMR(CDCl3)

delta (ppm):1.50 (s, 12H, -C3 (CH3)), -COC(CH3) CO-, 2.22 (s, and 3H and CH3CO-), 3.05 (s, 3H, -OSO2CH3), 4.50 (s, and 2H and -CH2-OSO2-)

13C-NMR(CDCl3)

delta (ppm):17.2 (CH3), and 27.2 (CH3), 27.5 (CH3), 36.9 (CH3), 59.9 (>C — <), 71.1 (>C — <), 83.1 (CH2), 168.3 (C=O) and 202.7 (C=O)

IR(cm⁻¹): 1738 (>C=O of ester) 2981, 1714 (>C=O)

Elemental-analysis C11H20O4Scalc. C:47.13% H:7.19% S:11.44%found C:47.33% H:7.45% It was made to react with 2-phenyl-2-propanol, having used sodium acetate as the catalyst, and example of S:10.3% reference 3 diketene was made into acetoacetic-acid 2-phenyl-2-propyl ester. The hydroxymethyl derivative obtained by performing methylation and methylol-ization like an example 1 in this was made to react with p-tosyl chloride, and 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid 2-phenyl-2-propyl ester was obtained as oily matter.

1H-NMR(CDCl3)

delta (ppm):1.39(s,3H,-COC(CH3)CO-),1.75(s,3H,-O-C(CH3)2-),1.79(s,3H,-O-C(CH3)2-),2.12(s,3H,CH3CO-),2.44 (s,3H,Ar-CH3),4.30(ABq,J=14Hz,2H,-CH2-OSO2-),7.30(s,5H,Ar-H),7.35(d,J=8.7Hz,2H,Ar-H),7.74(d,J=8.7Hz,2H,Ar-H)

IR(cm⁻¹): 1738 (>C=O of ester) 2983, 1716 (>C=O)

Elemental-analysis C22H26O6Scalc. C:63.14% H:6.26% S:7.66%found C:62.98% H:6.48% S:6.76% [0045] The methylol-ized acetoacetic-acid 2-phenyl-2-propyl ester which was obtained in the example of reference 4 example 3 was made to react with methane sulfonyl chloride, and 2-methyl-2-methane sulfonyloxy-3-keto butanoic acid 2-phenyl-2-propyl ester was obtained as oily matter.

1H-NMR(CDCl3)

delta (ppm):1.49(s,3H,-COC(CH3)CO-),1.75(s,3H,-O-C(CH3)2-),1.80(s,3H,-O-C(CH3)2-),2.20(s,3H,CH3CO-),2.90 (s,3H,-SO2CH3),4.48(dd,J=13Hz,2H,-CH2-O-),7.30(s,5H,Ar-H)

IR: 1738 (>C=O of ester) 2985, 1714 (>C=O)

The example of reference 51-methyl hexene was oxidized under existence of osmium oxide, and the cis-1-methyl 1 and 2-dihydroxy hexane were obtained. This was made to react under existence of p-tosyl chloride and triethylamine, and the cis-1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane was obtained at 82% of yield.

Colorless prism ** m.p.65-66 degree-CIR 3460, 2935, 1598, 1348, 1176cm⁻¹, 1 H-NMR delta= 1.1 (s, and 3H and -CCH3 (OH)-) (60MHz, CDCl3), (KBr) 1.9 (s, 1H, OH) 1.1-2.0 (m, 8H, -(CH2) 4-), 2.5 (s, 3H, Ar-CH3), 4.3 (ABq, 1H, and -CH(OTs)-, J = 5 or 9Hz), 7.4 (d, 2H, Ar-H, J= 8Hz), 7.8 (d, 2H, Ar-H, J= 8Hz)

[0046] The example of reference 62-methyl-3-hydroxy propene was oxidized by the tert-butyl hydroperoxide under existence of triphenyl phosphine, and the 1 and 2-epoxy-2-methyl-3-hydroxy propane was obtained. This was made to react with p-tosyl chloride under existence of triethylamine, and the 1 and 2-epoxy-2-methyl-3-(p-toluenesulfonyloxy) propane was obtained.

The colorless oily matter (NaCl) 1600 and IR 1364, 1192 or 1178cm⁻¹ 1 H-NMR (60MHz, CDCl3) delta= 1.3 (s, 3H, CH3), 2.5 (s, 3H, Ar-CH3), 2.9 (s, and 2H and -CH2O-), 7.4 (d, 2H, Ar-H, J= 8Hz), 7.8 (d, 2H, Ar-H, J= 8Hz)

After ketal-izing example of reference 7 benzoylacetacetic-acid ethyl ester by ethylene KURIKO-RU, it returned with p-toluenesulfonyl chloride and considered as the 3-phenyl-2 and 3-ethyl-1,2-dihydroxy propane-1, p-tosyl chloride was made to react to this under existence of triethylamine, and the crystalline 1-(p-toluenesulfonyloxy)-3-phenyl-3 and 3-ethylene dioxy propane were obtained with about 70% of yield.

Colorless oily matter m.p.48-50 degree-CIR 2892, 1597, 1354, 1178cm⁻¹, 1 H-NMR delta= 2.27 (t, 2H, -CH2CH2OTs, J= 8Hz) (90MHz, CDCl3), (KBr) 2.44 (s, 3H, Ar-CH3) and 3.6- 4.1 (m, 4H, and -OCH2CH2O-), 4.15 (t, 2H, -CH2CH2OTs, J= 8Hz), and 7.2- 7.5 (m, 7H, Ar-H) and 7.76 (d, 2H, Ar-H, J= 8Hz)

[0047] The 4-% of the weight cyclohexane solution of example 1 Pori (p-(tert-butoxycarbonyloxy) styrene) was prepared, and the diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate which is 5% of the weight (it is two-

mol % to a monomeric unit) of a photo-oxide generating agent was dissolved to this polymer. Addition of the 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester which is the acid growth agent obtained in the example 1 of reference in this solution was carried out to this polymer 10% of the weight (it is six-mol % to a monomeric unit). It considered as the thin film which carries out spin spreading of this solution on a silicon wafer, and has 0.5-micrometer thickness, and prebake processing was performed for this for 1 minute at 100 degrees C. For the comparison, the poly membrane which does not contain an acid growth agent was prepared similarly. These poly membranes were drawn for 7 minutes, and after changing time amount and carrying out UV irradiation of each, postbake processing was performed at 100 degrees C. Since the acid decomposed and thickness reduced this macromolecule, thickness change was measured and sensitization speed was evaluated. To the acidolysis of a macromolecule being completed by exposure for 17 seconds, when an acid amplification agent is added, in the acid growth agent additive-free case, in order for the reduction in thickness to be about 25% and to dissolve completely in the exposure for 17 seconds, the exposure for 50 seconds was required by the postbake for 2 minutes. Moreover, when an acid growth agent was added, reduction of the thickness in postbake has taken place rapidly, and the amplification effect was accepted clearly. Image formation was checked by carrying out postbake processing behind the bottom of exposure through a mask.

[0048] Instead of the diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate used as a photo-oxide generating agent in example 2 example 1, 6% of the weight of 2 and a 3-diphenyl-3-keto-2-hydroxy-1-(p-toluenesulfonyloxy) propane were added as a photo-oxide generating agent, and the addition effect of the 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester obtained in the example 1 of reference was investigated. After carrying out spin spreading of the thin film on a silicon wafer like an example 1, postbake was performed at 100 degrees C for 3 minutes after carrying out ultraviolet-rays exposure. In the acid growth agent additive-free case, although reduction of the thickness containing an acid growth agent was rapidly completed by the exposure for 60 seconds, by the same exposure time, thickness decreased only about 15%, but in order to complete thickness reduction, it required the exposure time for 180 seconds.

3.4% of the weight of triphenylsulfonium triflate and the 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester which is 1% of the weight of an acid growth agent were added to the cyclohexane solution of polymer used in the example 3 example 1 to polymer, and the thin film was prepared. After exposing ultraviolet rays, when postbake was performed at 100 degrees C for 3 minutes, the reduction in thickness was completed by the exposure for 55 seconds. In order in an additive-free case to remain in reduction of about 15% of thickness and to complete an acid growth agent by the same exposure time, the exposure time for 150 seconds was required.

[0049] 10% of the weight of diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate and the cis-1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane obtained in the example 5 of reference were added to the cyclohexane solution of polymer used in the example 4 example 1 5% of the weight to polymer, and on the silicon wafer, spin spreading was carried out and it considered as the 0.5-micrometer thin film. After performing postbake for 2 minutes at 100 degrees C after exposing ultraviolet rays, negatives were developed by ethanol, and the residual membrane was measured. Although all the films dissolved by the exposure time for 10 seconds when an acid growth agent was added, the exposure time for 70 seconds or more was required of additive-free.

The 1 and 2-epoxy-2-methyl-3-hydroxy propane compounded in the example 6 of reference instead of the cis-1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane used in example 5 example 4 was added. When UV irradiation, postbake processing, and ethanol development were performed similarly, the exposure time required in order to dissolve all films by adding an acid growth agent was able to be shortened to the quadrant.

[0050] 10% of the weight of diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate and the cis-1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane obtained in the example 5 of reference were added to 2:1 copolymers ($M_w=4.01 \times 10^4$, $M_w/M_n=1.74$) of example 6 methyl methacrylate and methacrylic-acid 2-phenyl-2-propyl ester 5% of the weight, and on the silicon wafer, spin spreading was carried out and it considered as the 0.23-micrometer thin film. After irradiating ultraviolet rays at this, postbake processing was performed for 2 minutes at 100 degrees C, negatives were developed by ethanol, and the remaining rate of membrane was measured. By adding an acid growth agent, the exposure time required for becoming residual membrane zero was able to be shortened to the quadrant. Same exposure, postbake, and ethanol development were performed using the 1-(p-toluenesulfonyloxy)-3-phenyl -3 and 3-ethylene dioxy propane which were compounded in the example 7 of reference instead of the cis-1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane used in example 7 example 6. By adding this acid growth agent, the exposure time for solubilizing all films was able to be shortened to about 1/3.

[0051] In the cyclohexanone solution of polymer used in the example 8 example 1, the diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate which is a photo-oxide generating agent, and the 1-(p-toluenesulfonyloxy)-3-phenyl -3 and 3-ethylene dioxy propane were added 10% of the weight to polymer, respectively, and on the silicon wafer of three sheets, spin spreading was carried out, respectively and it considered as the 0.25-micrometer thin film. After irradiating ultraviolet rays through the fenestera rotunda with a diameter of 3mm at these thin films, it heat-treated at 105 degrees C, 115 degrees C, and 125 degrees C. After the discoloration accompanying reduction in thickness appeared immediately as a round shape which is 3mm, the round shape increased with time amount. Postbake time amount until a diameter is set to 12mm was 30 seconds by 125 degrees C for 45 seconds at 115 degrees C in 105 degrees C for 7 minutes. This is because the acid generated with light is spread with heating within a poly membrane and acid generating by decomposition of an acid growth agent is caused one after another in connection with it. When an acid growth agent was not added, such reduction did not take place.

[0052] % of the 15-mol 1-(p-toluenesulfonyloxy)-3-phenyl -3 as two-mol % 2, and the 3-diphenyl-3-keto-2-

hydroxy-1-(p-TORUHEN sulfonyloxy) propane and the acid growth agent as a photo-oxide generating agent and 3-ethylene dioxy propane were added to the solution of 2-methoxy ethyl acetate of an example 9p-trimethylsilyloxy styrene homopolymer (5.35×10^4 , $M_w/M_n=1.69$). After carrying out spin spreading of this solution by 1000rpm on the silicon wafer and carrying out prebake for 30 seconds at 100 degrees C, time amount was changed, ultraviolet rays were irradiated and postbake was given for 30 seconds at 100 degrees C. When it was immersed for 10 seconds into ethanol and negatives were developed, the exposure time which a poly membrane solubilizes completely was shortened to about 1/3 compared with acid growth agent additive-free.

After adding 3% of the weight of diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate, and 3% of the weight of 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester to the cyclohexane solution of 1:1 copolymers ($M_w=5.15 \times 10^4$, $M_w/M_n=2.04$) of example 10 methyl methacrylate and glycidyl methacrylate to this polymer, spin spreading was carried out on the anodized aluminum board. To this, time amount was changed, ultraviolet rays were exposed, and after carrying out postbake at 100 degrees C for 3 minutes, the board was washed with toluene. When compared with the case where an acid growth agent is not added, the exposure time which insolubilization of a copolymer takes was shortened to 1/5.

[0053] Addition of the 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester which is the acid growth agent obtained in the example 1 of reference in the cyclohexane solution of polymer used in the example 11 example 1 was carried out to this polymer 10% of the weight (it is six-mol % to a monomeric unit). It considered as the thin film which carries out spin spreading of this solution on a silicon wafer, and has 0.27-micrometer thickness, and prebake processing was performed for this for 1 minute at 100 degrees C. For the comparison, the poly membrane which does not contain an acid growth agent was prepared similarly. 3.5% of the weight of triphenylsulfonium TORIFURA-TO was dissolved in the 0.07-% of the weight isopropyl alcohol solution of novolak resin to resin, and spin spreading was carried out on the poly membrane which prepared this previously. Prebaking for 1 minute at 100 degrees C, the film which consists of two-layer [of the film containing a photo-oxide generating agent and the film containing an acid growth agent] became the thickness of 0.62 micrometers as a whole. After exposing ultraviolet rays on this two-layer film, postbake processing was performed at 100 degrees C, and negatives were developed in 40-degree C ethanol for 1 minute. When asked for the relation between the exposure time and a remaining rate of membrane, having high-sensitivity-ized the two-layer film which added the acid growth agent 20 times compared with an additive-free two-layer film was admitted.

[0054] In example 12 example 11, when the completely same exposure as an example 10 was performed about the film of the two-layer structure which added triphenylsulfonium hexafluoroantimonate instead of triphenylsulfonium TORIFURA-TO as a photo-oxide generating agent, 18 times as many high sensitivity-ization as this was accepted by addition of an acid growth agent.

The sensitivity of the film of the two-layer structure which added the triphenylsulfonium hexafluoroantimonate prepared in the example 13 example 11, and the film which added triphenylsulfonium hexafluoroantimonate to the polymer of the example 1 which is a well-known chemistry amplification mold photoresist was measured. Consequently, the film of the two-layer structured type which separates and contains an acid growth agent showed 25 times as many high sensitivity as this to the chemistry amplification resist.

[0055]

[Effect of the Invention]

- (1) Since sensitization speed improves sharply, it can use for a high sensitivity image formation material.
- (2) Since the bridge formation effectiveness of photo-curing resin improves sharply by combining an optical exposure and heat-treatment, it can use to an ultraviolet curing mold coating, ink, a surface coating agent, etc. effectively. In the paint film which consists of a photo-curing agent which carried out pigment content powder, although it does not happen at all in that hardening is inadequate or the interior since light absorption happens only by the surface layer, according to this invention, hardening can be made perfect by heat-treatment after an optical exposure.
- (3) Since the yield of an acid increases sharply by the acid growth agent, it can reduce the amount of the photo-oxide generating agent used. Consequently, since light can fully permeate to the interior of a sensitization layer, it becomes possible to increase the thickness of a sensitization layer of it sharply.

[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公 開 特 許 公 報 (A)

(11) 特許出願公開番号

特開平8-248561

(43) 公開日 平成8年(1996)9月27日

(51) Int.Cl. ⁴	識別記号	庁内整理番号	F I	技術表示箇所
G 0 3 C	1/675		G 0 3 C	1/675
C 0 8 K	5/15	K F Y	C 0 8 K	5/15
	5/42			5/42
C 0 8 L	25/18	K G A	C 0 8 L	25/18
	33/12	L H Y		33/12
			審査請求 未請求	請求項の数 3 O L (全 12 頁)

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(54) 【発明の名称】 光反応性組成物、該光反応性組成物を含有した重合反応高分子組成物及び重合反応性樹脂層

(57) 【要約】
【目的】 本発明は、光反応速度の異なる光反応性組成物を提供することを目的とする。
【構成】 光の作用によって酸を発生する光酸発生剤と、酸光酸発生剤より発生した酸により新たに酸を発生する酸増殖剤とからなる光反応性組成物である。

【特許請求の範囲】
【請求項1】 光の作用によって酸を発生する光酸発生剤と、該光酸発生剤より発生した酸により新たに酸を発生する酸増殖剤とからなる光反応性組成物。

【請求項2】 酸の作用によって分子構造変化を生じる物質を混合した高分子物質、あるいは酸の作用によって分子構造変化を生じる残基を結合した高分子物質中に、光の作用によって酸を発生する光酸発生剤と、酸増殖剤とによって新たに酸を発生する酸増殖剤を存在せしめたことを特徴とする酸反応性高分子組成物。

【請求項3】 酸の作用によって分子構造変化を生じる物質を混合した高分子物質、あるいは酸の作用によって分子構造変化を生じる残基を結合した高分子物質と光酸発生剤とからなる樹脂層に、前記光酸発生剤より発生した酸の作用によって分子構造変化を生じる物質を混合した高分子物質、あるいは酸の作用によって分子構造変化を生じる残基を結合した高分子物質からなる前記の樹脂層とは異なる樹脂層を積層した2層構造を有する酸反応性樹脂層。

【発明の詳細な説明】

【0001】
【産業上の利用分野】 本発明は、光の作用で酸を発生する物質（以下、光酸発生剤と呼ぶ）に、発生した酸によって新たに酸を発生する物質（以下、酸増殖剤と呼ぶ）を組み合わせてることにより感光速度を向上させた光反応組成物に関し、更に、該光反応組成物を含有した酸反応性高分子組成物及び酸反応性樹脂層に関する。

【0002】

【従来の技術】 従来より光エネルギーを吸収して分子内又は分子間に化学的又は物理的変化を生じる感光性機能を有する材料は種々の方面に利用されている。例えば、光反応によって生じる化学的な構造変化を光学的に検出する画像形成材料として用いたり、モノマーやプレポリマーの光硬化によって表面処理を行う表面被覆処理材料として用いるなど、多方面に利用、実用化されている。しかし、これらの感光性機能を有する材料における感光速度、感光感度領域、解像性は多様であり、目的に応じて適切な特性を有する材料が選択される。

【0003】 感光性機能を有する材料として古くより銀塩感光材料が広く用いられているが、近年、写真製版技術などにおけるように、大量、かつ、高解像性を示す高感度画像形成材料として、高分子材料を主成分とする感光性樹脂が広範囲にわたって用いられるようになった（山岡 亜夫、松永元太郎編、「フोटポリマー・テクノロジ-」、日刊工業新聞社（1988年）参照）。高分子系感光性材料は解像性に優れているだけでなく、光反応の選択によって広範囲の感光感度領域が設定できる。また、比較的安価に製造できるなどの多くの利点を有する。しかしながら、感光速度は銀塩感光材料に比

較するときわめて低く、最も高感度な高分子系感光性材料とさえども、銀塩に劣る感光速度の乏しみの一にも違いないのが現状である。

【0004】 これまでに、高分子系感光性材料の感光速度を向上させるために、さまざまな試みがなされてきた。最も広く開発の外れとなってきたのが、光の作用で発生するラジカル種、開始剤として、多数のニルモノマーを連鎖的に重合させる光重合体系である。しかしながら、空気中の酸素と容易に反応するラジカル種が成長種であるために、十分な連鎖反応が完了することなく封鎖される。また、ラジカル重合反応の進行とともに急速に形成される高分子ラジカル種内での鎖目閉鎖のために、モノマーの拡散が急速に抑制されて重合が完了することができない。このような原因のために、光重合系の感光速度には本質的な限界値が存在する。

【0005】 一方、光の作用で酸を発生させる、この酸を触媒とするカチオン、含のみならず、さまざまな酸触媒反応を組み合わせてることによって、多様な高分子系感光性材料の創出が可能となった。カチオン重合において、ラジカル重合とは異なり触媒による反応の停止効果が無いので高感度が可能であるが、実際には空気中の水分や鎖目構造形成のために、むしろラジカル重合系よりも感光速度は低いのが現状である。また、酸触媒反応を組み込んだ高分子系感光性材料では、光で酸を発生させた後に加熱処理を施して酸触媒反応を誘起させることを原理とする。このため、フोटレジストを主たる利用形態とするこの種の高分子系感光性材料は化学増幅型フोटレジストと呼ばれている。しかし、依然として感光速度はラジカル重合系にも及ばないのが現状であり、飛躍的な感光速度の向上が求められてきた。

【0006】 更に、光ラジカル重合やカチオン重合を用いたり、あるいは別の両者を組み合わせることによって、諸族あるいは酸・引当酸を光源で高感度に硬化する樹脂組成物も広く実用に供せられている。近年、空気中の酸素による阻害効果を受けないカチオン重合系は広く開発研究の对象となっており、硬化に致した光酸発生剤や硬化に適用したモノマーやプレポリマーの間接は活発に行われているが、硬化工程の迅速化のために硬化速度の向上が求められている。さらには、光を吸収する原料が分散した樹脂、成物や厚い膜の硬化は表面層のみで起こるために、十分な硬化がもたらされないという本質的な問題点は解かれ、されにまで至っている。また、前述の化学増幅型フोटレジストの感光速度が、酸触媒反応を利用しているにもかかわらず、それほど高いものとならない原因として、空気中に再遊する微量の塩基成分が触媒の放出、用をもちたためと考えられ、或いは、高分子ラジカル種中の酸触媒反応が副反応を引き起こし、このため酸触媒反応が停止することも考えられる。

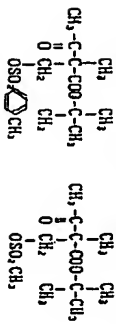
【0007】

(5)

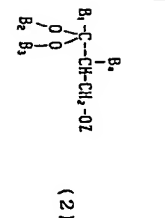
い、酸の残基で置換された化合物であって、比較的容易に脱酸反応を引き起こして、酸を発生する化合物である。

したがって、脱酸反応によって、この脱酸反応は大幅に活性化させることができ、酸の存在下では安定であるが、酸の存在下では容易に熱化学反応によって酸を生成させることが可能となる。このような性質を持つ脱酸増進剤を、光酸発生剤と組み合わせて、これによって、限定的に脱酸速度が向上された光反応性組成物が可能となったのである。脱酸反応によって分解して再び酸（以下の一般式でZOH）を発生する。一回の反応で1つ以上の酸が脱えておき、反応の進行に伴って加速的に反応が進む。発生した酸自体が自己分解を誘起するために、ここで発生する酸の強度は脱酸増進剤、PKa、として3以下であり、とくに2以下であることが望ましい。これより弱い酸であれば、自己分解を引き起こすことができな

い、このような酸として、ジクロロ酢酸、トリクロロ酢酸、メタンスルホン酸、エタンスルホン酸、ベンゼンスルホン酸、p-トルエンスルホン酸、ナフタレンスルホン酸、トリフェニルホスホン酸などをあげることができ、具体的に、以下の化合物を例示することができ、第1に、一般式(1)で表される有機酸エステル化



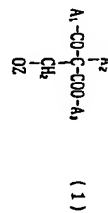
[0021] 第2に一般式(2)で表されるアセタールまたはケタール基を持つ有機酸エステルを挙げることができ、



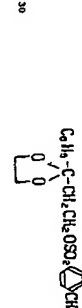
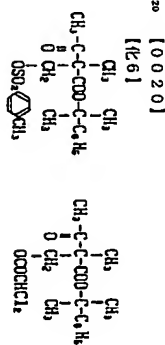
[0023] (式中、Zは前記と同じ意味を持ち、B1は水素原子、アルキル基またはアリール基であり、B2、B3はメチルあるいはエチル基または同音でエチレンまたはプロピレン基を形成し、B4は水素原子またはメチル基を示す)
この化合物は酸の作用でアセタールあるいはケタールが分解してβ-アルデヒドあるいはケトンとなり、これからZOHが容易に脱離する。具体的な例を以下に示す。
[0024]
[化8]

* 化合物を挙げることができる。

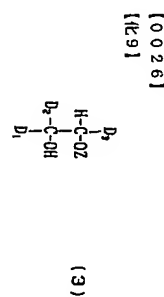
[0018]
[化5]



[0019] (式中、A1はC1からC6までのアルキル基またはアリール基を示し、A2はC1からC6までのアルキル基を示し、A3はビス(p-アルコキシジエニル)メチル)基、2-アルキル-2-プロピル基、2-アリール-2-プロピル基、シクロヘキシル基またはテトラヒドロピラニル基を示し、Zは脱酸増進剤(PKa)が3以下であるZOHで示される酸の残基を示す)この化合物に酸が作用すると、エステル基が分解してカルボン酸となり、これがさらに脱カルボン酸を起してから酸(ZOH)が容易に脱離する。具体的な例を以下に示す。

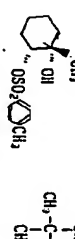


[0025] 第3に、一般式(3)で表される有機酸エステルを挙げることができる。

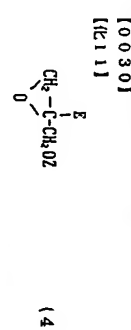


[0027] (式中、Zは前記と同じ意味を持ち、D1、D2は水素原子、C1からC6までのアルキル基またはアリール基を示し、D2、D3はC1からC6までのアルキル基または双方で脂環状構造を形成するアルキレンあるいは置換アルキレン残基を示す)

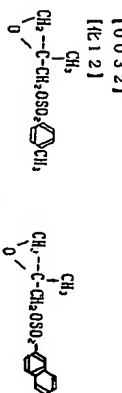
この化合物は、酸触媒によって水酸基が脱離してカルボカチオンを形成し、水素移動してからZOHが生成するものと推定される。具体的な例を以下に示す。



[0029] 第4に、一般式(4)で表されるエポキシ環を有する有機酸エステルを挙げることができる。



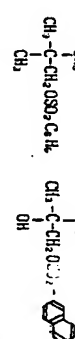
[0031] (式中、Zは前記と同じ意味を持ち、EはC1からC6までのアルキル基またはフェニル基を示す)この化合物に酸が作用すると、エポキシ環の開環の生成に伴ってβ-炭素にカチオンが形成され、水素移動の結果として有機酸が発生するものと推定される。具体的な例を以下に示す。



[0033] これらの化合物は酸が作用しない限り室温で安定に存在する。これらの化合物の脱酸増進剤が引き起こされるためには一定以上の酸強度が必要とされるが、脱酸増進剤PKaで約2以下であることが望ましい、これ以上の脱酸増進剤、すなわち、これ以上に弱い酸であれば、脱酸増進剤の反応を引き起こすことができな

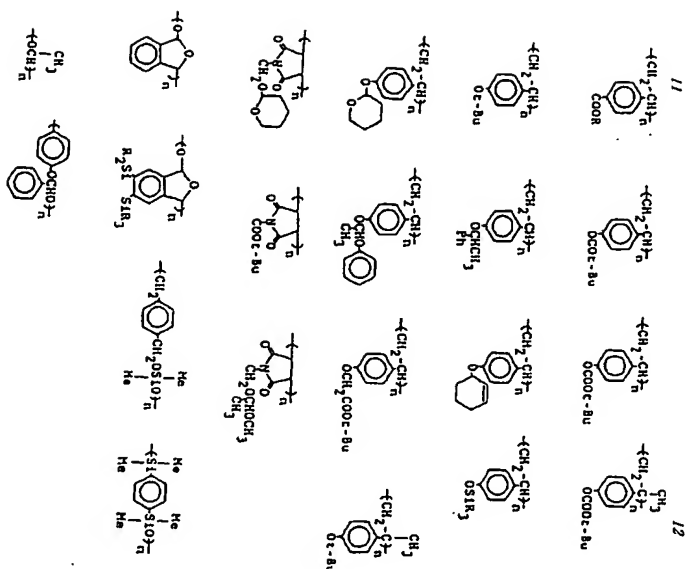
(6)

* [0028]
[化10]



[0034] 次に、上記光反応性組成物を存在させる酸の作用によって分子構造に変化を生じる物質(酸反応性分子)を融合した高分子物質、あるいは酸の作用によって分子構造変化を生じる物質を融合した高分子物質について説明する。なお、分子構造変化を生じる物質又は残基を単に酸反応性分子又は酸反応性残基と言う。本発明に好適に用いられる酸反応性分子を融合あるいは結合してなる高分子物質の例を示す(有機エレクトロニクス材料研究会編、「イメーシング用有機材料」、ぶんしん出版(1993年)、199~201ページ参照)。多くは有機合成化学における保護基の反応を利用している(T. W. Greene, Protective Groups in Organic Synthesis, John Wiley & Sons (1981)参照)が、具体的な例を以下に示す。第1に、酸反応性残基を側鎖あるいは主鎖に有する高分子物質を挙げることができ、酸反応性残基としては、カルボン酸の第2位、第3位エニル基、テトラヒドロピラニルエニル基、炭酸第3位エニル基、トリアルキルシリル基やテトラヒドロピラニル基で置換されたフェニル性あるいはN-メチロール性水酸基が好適に用いられる。これらは、酸の作用によって脱保護反応が起こって断端の高いカルボン酸やフェノールが生成するので、断端部は断端性溶媒やアルカリ水溶液に可溶化する。このような特性を利用したのとして、高酸度溶媒材料がある。具体的な化合物の例として、

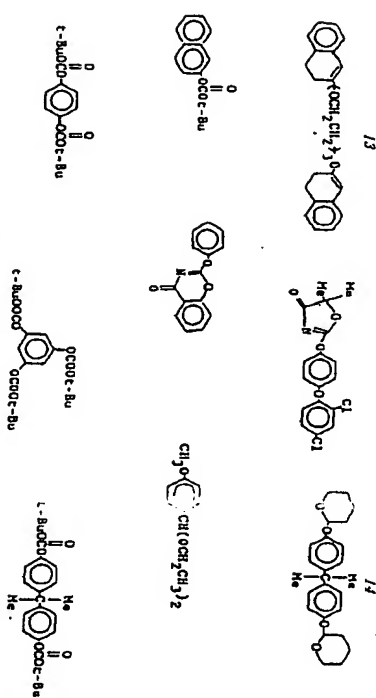
[0035]
[化13]



[0036] 第2に、酸反応性低分子化合物を含有する高分子化合物の溶解性を低減する効果をもたらすものである。溶媒如油類と呼ばれる、溶媒如油類として、アセトアル化合物、ケトアル化合物、カルボ酸の第3級エステル、テトラヒドロピルニルエステル、炭酸第3級エステル、トリアルキルシリル基やテトラヒドロピルニル基で置換されたフェノール類、ヒナミン等様々なものを挙げることができる。これらの溶媒如油類を含有する樹脂は樹脂として、たとえば、ノボラック樹脂、ポリ（p

ーヒドロキシスチレン)、メタクリル酸共重合体、N-メチロールアミド共重合体とをあげることができる。低分子化化合物はこれらの樹脂のアルカリ水溶液に対する溶解性を阻害する効果を持つが、酸の作用で分解することによって、この溶解阻害効果が失われ低分子化はアルカリ可溶化となる。具体的な溶解阻害剤を以下に例示する。

【0037】
【化14】



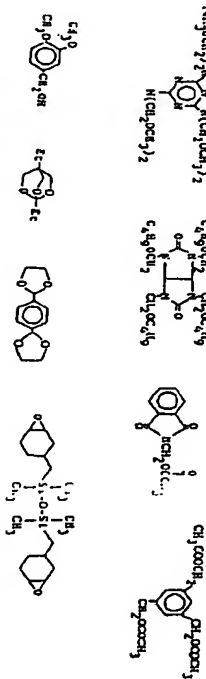
【0038】第3に、酸触媒反応による場合反応速度は高分子の架橋反応に利用する。酸触媒として、ベンジルトリコール、アセトール誘導体、ピニルエチル誘導体などを用いることができる。また、生成したカチオンと反応する誘導体としては、フェノール、アルコールなどを挙げるこ

*とがき、これらの構造を有する成分、たとえば、 P —ヒドロキシスチレンの重合体、ノボラック樹脂、ヒドロキエチルメタクリレートの重合体、が好適に用いられる。縮合反応によりこの化合物を以下に例示する。

[0039]

[化15]

20



【0040】また、この縮合性基とフェニル樹脂を合わせた高分子は、それ自体で樹脂類によって架橋を起すので、本発明に都合がよい。第4に、樹脂類に

することが好ましい。

【0004】 について、本発明の感光性樹脂組成物の調整方法を以下に述べる。酸反応性単位を持つ低分子物質を含む樹脂あるいはそれ自体が酸反応性である高分子化合物に、それに對して0.5～20重量%の光酸発生剤、および、0.1～20重量%の酸増強剤を添加する。上記の光酸発生剤の多くは酸とともに、ラジカル種

を発生するので、 β -反応性物質とともに、ラジカル重合性モノマーやポリマーを重合することもできる。さらには、顔料、染料などを適量添加してもよい。

[00042] 均一に分散するために、それぞを溶媒に溶解することがあり、ましい。これらの組成物を膜状に形成して塗料、としての膜を発生させる。ついで、加熱（ガス・トーチ）処理を行って膜形成剤の速激的な分解を促すとともに、酸触媒反応によって酸反応性物質の構造変化を引き起こす。加熱処理の条件は、露光エネルギー、用いる酸、活性な残基の種類、高分子の種類、などによって変動するが、加熱温度は60度から150度の範囲、時間より短く、しくは80度から130度の範囲である。加熱時間、より短く、しくは10分、より長くは30秒から5分。この上、加熱時間が短く、酸触媒反応が十分には引き起こさない。この範囲を越える時間では酸触媒剤が副反応、を引き起こす場合があるし、また、生成体に欠ける。酸反応性物質を含む材料あるいは、それ自体が酸反応性である樹脂の構造変化に伴う露光と加熱処理の相関性、速度、効率、

理前後における、主、たとえば、溶解性、硬度、強度、

15 活性、反応発生物の変化を利用する。更に本発明においては光増殖剤を含む樹脂層と、酸増殖剤を含む樹脂層とに分けて2層構造とすることができ、次に実施例をもつて更に具体的に本発明を説明する。

[0043]

【実施例】まず本発明で使用する代表的な酸増殖剤の合成例を参考例として示す。

参考例1

アセト酢酸フェリニブチルエニルをTHF中水酸化ナトリウムの存在下でヨウ化メチルと反応させて得た2-メチル-3-オクトザン酸フェリニブチルエニルに水酸化カリウムの存在下でエタノール中でホルミリンと反応させた、収率40%で生成した2-ヒドロキシメチル-2-メチル-3-オクトザン酸フェリニブチルエニルをジクロロメタン中でトリエチルアミンの存在下でp-トルエンホルミルクロリドと反応させて、2-メチル-2-(p-トルエンホルミルオキシ)-3-オクトザン酸フェリニブチルエニルを油状物として得た。生成物はシリカゲルカラムクロマトグラフィーで精製した。

mp. 52~53℃

¹H-NMR (CDCl₃)

δ (ppm) : 1.38 (s, 3H, -COC (C H₃) CO-), 1.40 (s, 9H, -C (C H₃) CO-), 2.15 (s, 3H, CH₃CO-), 2.47 (s, 3H, Ar-CH₃), 4.28 (ABq, J=10Hz, 2H, -CH₂-OSO₂-), 7.38 (d, J=7.7Hz, 2H, Ar-H), 7.77 (d, J=7.7Hz, 2H, Ar-H)
IR (cm⁻¹): 3000, 1738 (エニルの>C=O), 1719 (>C=O)
元素分析 C₁₇H₂₄O₆S
calc. C: 57.29% H: 6.79% S: 9.00%
found C: 57.18% H: 6.90% S: 8.84%

[0044] 参考例2

実施例1と同様に、p-トルエンホルミルクロリドの代わりにメタンスホルミルクロリドを用いて、2-メチル-2-メタンスホルミルオキシ-3-オクトザン酸フェリニブチルエニルを油状物として得た。

¹H-NMR (CDCl₃)

δ (ppm) : 1.50 (s, 12H, -C (C H₃) CO-), -COC (CH₃) CO-, 2.22 (s, 3H, CH₃CO-), 3.05 (s, 3H, -OSO₂CH₃), 4.50 (s, 2H, -CH₂-OSO₂-)
¹³C-NMR (CDCl₃)
δ (ppm) : 17.2 (CH₃), 27.2 (C H₃), 27.5 (CH₃), 36.9 (CH₃), 5

(9)

16

9.9 (>C<), 71.1 (>C<), 83.1 (C H₂), 168.3 (C=O), 202.7 (C=O)
IR (cm⁻¹): 2981, 1738 (エニルの>C=O), 1714 (>C=O)
元素分析 C₁₁H₂₀O₄S
calc. C: 47.13% H: 7.19% S: 11.44%
found C: 47.33% H: 7.45% S: 10.3%

参考例3

ジブチルを酢酸ナトリウムを触媒として2-ブチル-2-ブチルと反応させてアセト酢酸2-ブチル-2-ブチルエニルとした。これを実施例1と同様にメチル化、メチル化を行い、得られたヒドロキシメチル誘導体をp-トルエンホルミルクロリドと反応させて、2-メチル-2-(p-トルエンホルミルオキシ)-3-オクトザン酸2-ブチル-2-ブチルエニルを油状物として得た。

¹H-NMR (CDCl₃)

δ (ppm) : 1.39 (s, 3H, -COC (C H₃) CO-), 1.75 (s, 3H, -O-C (C H₃) CO-), 1.79 (s, 3H, -O-C (C H₃) CO-), 2.12 (s, 3H, CH₃CO-), 2.44 (s, 3H, Ar-CH₃), 4.30 (ABq, J=14Hz, 2H, -CH₂-OSO₂-), 7.30 (s, 5H, Ar-H), 7.35 (d, J=8.7Hz, 2H, Ar-H), 7.74 (d, J=8.7Hz, 2H, Ar-H)
IR (cm⁻¹): 2983, 1738 (エニルの>C=O), 1716 (>C=O)
元素分析 C₂₂H₂₆O₆S
calc. C: 63.14% H: 6.26% S: 7.66%
found C: 62.98% H: 6.48% S: 6.76%

[0045] 参考例4

実施例3で得たメチル化したアセト酢酸2-ブチル-2-ブチルエニルをメタンスホルミルクロリドと反応させて、2-メチル-2-メタンスホルミルオキシ-3-オクトザン酸2-ブチル-2-ブチルエニルを油状物として得た。

¹H-NMR (CDCl₃)

δ (ppm) : 1.49 (s, 3H, -COC (C H₃) CO-), 1.75 (s, 3H, -O-C (C H₃) CO-), 1.80 (s, 3H, -O-C (C H₃) CO-), 2.20 (s, 3H, CH₃CO-), 2.90 (s, 3H, -OSO₂CH₃), 4.48 (dd, J=9.0Hz, 2H, -CH₂-O-), 7.30 (s, 5H, Ar-H)
IR: 2985, 1738 (エニルの>C=O), 1

17

714 (>C=O)

参考例5

1-メチルヘキセンを酸化オキシムラムの存在下で酸化してシス-1-メチル1, 2-ジヒドロキシヘキセンを得た。これをp-トルエンホルミルクロリドとトリエチルアミンの存在下で反応させて、収率82%でシス-1-メチル-1-ヒドロキシ-2-(p-トルエンホルミルオキシ)-ヘキセンを得た。

無色油状物 mp. 65~66℃

IR (KBr): 3460, 2935, 1598, 1348, 1176 cm⁻¹, ¹H-NMR (60MHz, CDCl₃) δ=1.1 (s, 3H, -CCH₃(OH)-), 1.9 (s, 1H, OH), 1.1-2.0 (m, 8H, -CH₂-), 2.5 (s, 3H, Ar-CH₃), 4.3 (ABq, 1H, -CH(OT s)-), J=5.9Hz), 7.4 (d, 2H, Ar-H), J=8Hz), 7.8 (d, 2H, Ar-H, J=8Hz)。

[0046] 参考例6

2-メチル-3-ヒドロキシブチルをトリブチルホスファインの存在下でフェリニブチルとヒドロキシクロロベンゼンを得た。これをトリエチルアミンの存在下でp-トルエンホルミルクロリドと反応させて、1, 2-エポキシ-2-メチル-3-(p-トルエンホルミルオキシ)ブチルを得た。

無色油状物

IR (NaCl): 1600, 1364, 1192, 1178 cm⁻¹
¹H-NMR (60MHz, CDCl₃) δ=1.3 (s, 3H, CH₃), 2.5 (s, 3H, Ar-CH₃), 2.9 (s, 2H, -CH₂O-), 7.4 (d, 2H, Ar-H, J=8Hz), 7.8 (d, 2H, Ar-H, J=8Hz)。

参考例7

ペンゾイル酢酸エチルエニルをエチレングリコールによってエステル化してから、水酸化リチウムニシラで還元して3-ブチル-3, 3-エチレンジオキシブチル-1とした。これをp-トルエンホルミルクロリドとトリエチルアミンの存在下で反応させて、結晶性の1-(p-トルエンホルミルオキシ)-3-ブチル-3, 3-エチレンジオキシブチルを約70%の収率で得た。

無色油状物 mp. 48~50℃

IR (KBr): 2892, 1697, 1364, 1178 cm⁻¹, ¹H-NMR (90MHz, CDCl₃) δ=2.27 (t, 2H, -CH₂CH₂OT s, J=8Hz), 2.44 (s, 3H, Ar-CH₃), 3.6-4.1 (m, 4H, -OCH₂CH₂O-), 4.15 (t, 2H, -CH₂CH₂OT s, J=8Hz), 7.

(10)

18

2-7.5 (m, 7H, Ar-H), 7.76 (d, 2H, Ar-H, J=8Hz)。

[0047] 実施例1

ポリ(p-フェリニブチルオキシ)スチレンの少量%シクロヘキサン溶液を調製し、このポリマーに対して5.1重量% (モノマー単位に対して2モル%) の光増殖剤であるジブチル(p-ブチルオキシ)スチレン・ヘキサフルオロエチルオキシを溶解した。この溶液を参考例1で得た酸増殖剤である2-メチル-2-(p-トルエンホルミルオキシ)-3-オクトザン酸フェリニブチルエニルをこのポリマーに対して1.1重量% (モノマー単位に対して6モル%) 添加した。この溶液をシリコンエナートにスピン塗布して0.5mmの膜厚を持つ薄膜とし、これを100℃で1分間ブリーチ処理を行った。比較のために、酸増殖剤を含まない高分子膜を同様にして調製した。これらの高分膜を7分間、それぞれを時間を逐えて紫外線照射して、100℃でポストベーク処理を行った。この高分膜は酸によって分解して膜厚が減るので、膜厚変化を測定して感光速度を評価した。2分間のポストベークによって、酸増殖剤を添加した場合に17秒感光で部分の感光分解は完結しているのに対して、酸増殖剤無添加の場合には、膜厚の減少は17秒の感光では約25%留まり、完全に溶解するためには50秒の感光を要し、また、酸増殖剤を添加した場合にポストベークにおける膜厚の減少は急激に起こっており、増殖効果が明かに認められた。マウスを通して露光後、ポストベーク処理をすることによって、面像形成が確認された。

[0048] 実施例2

実施例1において、光増殖剤として使用したジブチル(p-ブチルオキシ)スチレン・ヘキサフルオロエチルオキシの代わりに、6重量%の2, 3-ジブチル-3-オクトザン酸フェリニブチルエニル(p-ブチルオキシ)ブチル-3, 3-エチレンジオキシブチル-1を用いた。実施例1と同様にシリコンエナートにスピン塗布した。酸増殖剤を含有する膜の減少は60秒の露光で急激に完結したが、酸増殖剤の添加の場合には、膜厚は同じ露光時間では約15%減少しておらず、膜厚減少が完結するためには180秒の露光時間を要した。

実施例3

実施例1で用いたポリマーのシクロヘキサン溶液に、ポリマーに対して3.1重量%のトリブチルエニル・トリブチル・ヘキサフルオロエチルオキシ(p-ブチルオキシ)スチレン・ヘキサフルオロエチルオキシ)スチレンを添加した。この溶液を参考例1で得た酸増殖剤である2-メチル-2-(p-トルエンホルミルオキシ)-3-オクトザン酸フェリニブチルエニルを加えて露光を照射

